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COMBINED SHOCK-WAVE SYNTHESIS OF NOBLE SPINEL AND LAVES CUBIC PHASE

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The paper described the shock-wave synthesis of high-pressure high-temperature mineral $MgAl_2O_4$ with the parameter a = 8.085(3) Å and the Laves phase $MgCu_2$ with a = 7.076(2) Å from a mixture of MgO and aluminum powder placed into a copper insert inside a steel conservation ampoule. Spinel $MgAl_2O_4$ with a smaller lattice parameter a = 8.0798 Å has been formed in an aluminum insert cup.

We have earlier [1] synthesized mineral hercynite $FeAl_2O_4$ under shock-wave impact on gibbsite under axis-symmetric loading [2]. Later [3] we used the same method to grow crystals of mineral gahnite $ZnAl_2O_4$ and nonstoichiometric aluminozinc spinel $Zn_{0.33}Al_{2.45}O_4$ from amorphous aluminum hydroxide and zinc penetrating the reaction zone from the protective brass wall of the conservation ampoule. The tetrahedral positions in the structure of this phase are taken by 1/3 zinc atoms and 2/3 aluminum atoms $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$ [4]. In [5] we used the shock-wave impact on zincite placed into a thick-walled aluminum insert cup positioned along the axis of the steel conservation ampoule and thus synthesized aluminum oxide with a spinel structure according to the reaction $2Al + 3ZnO \rightarrow \sigma\text{-}Al_2O_3 + 3Zn$ [6]. Gibbsite $Al(OH)_3$ protected by the aluminum insert cup from reacting with iron under the same conditions forms two aluminum oxides: $\sigma\text{-}Al_2O_3$ and $\alpha\text{-}Al_2o_3$. The amount of the $\sigma\text{-}Al_2O_3$ phase is significantly larger [7]. This indicates that it is formed due to an additional reaction of water with the aluminum wall of the protective insert cup.

The present study shows the results of x-ray phase analysis of phases formed under shock-wave impact on a mixture of MgO and aluminum powder taken in the equimolar ratio (MgO : Al = 1 : 1). The conservation ampoule design did not differ from the one described in [3], with one exception: instead of the brass insert protecting the reaction mixture from reacting with the steel wall of the conservation ampoule, we took a copper insert of the same size.

Shock-wave loading, similarly to [1, 3 – 7], was performed by a sliding detonation wave from the explosion of a trotyl-hexogen charge 40/60 of density 1.672 g/cm^3 placed in an additional steel shell. The detonation velocity was 8100 m/sec, and the detonation pressure 26 GPa. X-ray phase analysis was performed under monochromatic Cu$K_{\alpha 1}$ radiation in a STADI-P autodiffractometer in a FR-552 monochromatic chamber (with germanium as the reference standard).

Analysis of the x-ray data indicates that as a result of the pulse impact of the intense shock wave on the prepared mixture, the components react not only with each other but with the copper insert as well. During a very short period of the shock wave effect $(2 – 5) \times 10^{-6}$ sec two phases with a face-centered cubic lattice were formed, namely noble spinel $MgAl_2O_4$ and the Laves cubic phase $MgCu_2$. Their structures are described in nonsymmorphic Fedorov symmetry group Fd_3m, in which magnesium atoms take position 8*a*, whereas aluminum and copper atoms take position 16*d*. Aluminum, copper, and magnesium crystals are subordinated to symmorphic group Fm3m. If its coordination symmetry planes *m* are replaced by sliding reflection planes *d* and the latter are shifted 1/8 along the cubic edges *a*, *b*, and *c*, then group Fd3m is formed. Nonsymmorphic groups can be regarded as superstructural subgroups of symmorphic spatial groups. All transformations of group Fd3m occur within group Fm3m [8]. Table 1 lists experimental x-ray data of synthesized compounds.

The parameter a of the elementary cell of noble spinel $MgAl_2O_4$ calculated based on Table 1 data is equal to 8.085(3) Å. This value differs little from the value published in [9] for normal spinel $MgAl_2O_4$. When the copper insert was replaced by an aluminum insert, spinel $MgAl_2O_4$ was formed with a smaller lattice parameter: a = 8.0798 Å. In the Laves cubic phase $MgCu_2$, a = 7.076(2) Å. This is slightly larger than the lattice parameter a published in [10].

When studying the products of the chemical reactions occuring at the front of the detonation wave with a MBS-9 microscope, we identified six transparent crystals. These crystals were subjected to x-ray spectral microscopy and

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TABLE 1

Intensity	Interplanar distance, Å	
	$MgCu_2$	$MgAl_2O_4$
6	–	4.6700
65	4.0860	–
13	–	2.8592
9	2.4989	–
20	–	2.4354
100	2.1313	–
47	2.0429	–
16	–	2.0199
8	1.7689	–
3	–	1.6509
10	–	1.5568
18	–	1.4288
20	1.3621	–
10	1.2507	–

were identified as aluminum oxide Al_2O_3. They were not suitable for x-ray structural study. It can be assumed that the following independent chemical reactions take place in the copper insert of the ampoule under the shock-wave effect:

$$2Al + 3MgO \rightarrow Al_2O_3 + 3Mg;$$

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4;$$

$$Mg + 2Cu \rightarrow MgCu_2;$$

$$2Al + 4MgO + 6Cu \rightarrow MgAl_2O_4 + 3MgCu_2.$$

Thus, using the shock-wave compression of three compounds with the spatial symmetry group Fm3m, we performed for the first time a simultaneous synthesis of two compounds with the same Fedorov group Fd3m: high-pressure high-temperature mineral $MgAl_2O_4$ and high-density ($5.780\ g/cm^3$) Laves cubic phase $MgCu_2$. The less dense intermetallic compound Mg_2Cu was not formed in the experiment. It can be assumed that $MgAl_2O_4$ and $MgCu_2$ are coherently coupled phases with a face-centered cubic lattice [11].

Consequently, using axis-symmetric shock-wave impact, it is possible to simultaneously modify the thermal and elastic components of the internal energy of the reacting mixture components within such wide limits that reactions can be performed and high-pressure crystal phases synthesized within a very short time (10^{-6} sec).

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